REMARKS

I. Interview Summary

Applicant thanks Examiner Vasisth for the time and courtesy extended in conducting a telephonic interview with Applicant's representative on March 1, 2011. During the interview, the rejection under 35 U.S.C. § 103(a) over U.S. Patent No. 6,736,991 to Cohen et al. ("Cohen") in view of U.S. Patent 6,231,782 to Shimomura et al. ("Shimomura") were discussed. Specifically, Applicant's representative explained that Cohen and Shimomura fail to disclose or suggest the combination of the specific mineral oil, phophorothionate, and phosphoric acid ester as claimed, and also discussed the unexpected beneficial results presented in Table 2 of the specification and the Rule 132 Declaration of Mr. Shimomura submitted with the Reply to Office Action filed November 16, 2009. No formal agreement was reached. The foregoing amendment and the following remarks reflect the substance of the interview.

II. STATUS OF THE CLAIMS

Applicant has cancelled claims 1 and 4-12, and has added new claim 13. The new claim is supported by the as-filed specification, e.g., paragraphs [0021], [0046], [0049], and Examples 1-6. No new matter has been introduced.

Claim 13 is pending and under examination.

As an initial matter, cancellation of claims 1 and 4-12 renders the rejection of these claims moot.

III. New claim 13

Applicant respectfully submits that new claim 13 is allowable over Cohen and Shimomura, considered alone or in combination, for at least the following reasons.

A reasonable expectation of success is required to support a conclusion of obviousness. M. P.E.P. § 2143.02. In order to have a reasonable expectation of success, at least some degree of predictability is required. M.P.E.P. § 2143.02(II). Applicant respectfully submits that the refrigerating machine oil as recited in claim 13 shows the unexpected beneficial results that were not predicted in the cited references, as discussed during the interview.

The present application discloses Examples 4-6, which correspond to the refrigerating machine oil recited in claim 13. *See* as-filed specification, paragraph [0129]. Specifically, the refrigerating machine oil compositions of Examples 4-6 each includes a combination of the mineral oil, phophorothionate, and phosphoric acid ester as recited in claim 13. As shown in Tables 2-3, Examples 4-6 (according to the claimed composition) showed marked improvement in wear resistance from the synergistic effect of the combination of the phophorothionate (A2) and the phosphoric acid ester (A1), as compared with Example 15, which included only the phosphoric acid ester (A1), and Example 16, which included only the phophorothionate (A2).

As discussed during the interview, these unexpected beneficial results would not have been achieved or predicted by Cohen or Shimomura. First, neither of the references discloses or suggests the combination of phosphorothionate and phosphoric acid ester as claimed. Cohen at column 7, line 3-5, discloses anti-wear compounds for refrigeration [being] alkyl-aryl or tri-aryl phosphates," but fails to disclose or suggest the specific combination of phosphorothionate and phosphoric acid ester. Shimomura at col. 9, lines 25-31 discloses several phosphorous compounds to be added to a refrigerating machine oil composition, but fails to disclose or suggest the combination of

phosphorothionate and phosphoric acid, as claimed. In the absence of this feature, neither Cohen nor Shimomura would lead one of ordinary skill in the art to arrive at the claimed invention and predicted the above-discussed beneficial results.

Regarding the claimed mineral oil, the Office Action asserted that Cohen at col. 3 lines 37-40 discloses naphthenic mineral oils and these mineral oils can be hydrotreated or refined to reduce sufur and nitrogen-containing compounds such that "the sulfur and nitrogen compounds have been reduced such that the total sulfur and nitrogen is low at levels 0.05% or less and the %C_A of the naphthenic mineral oil." Office Action at 3. During the interview, the Examiner continued to assert that Cohen's mineral oils encompass the mineral oil as claimed, and noted that concentrations of sulfur and nitrogen, and %C_A can be adjusted independently, and thus a decrease in sulfur content would not affect %C_A.

Applicant respectfully disagrees. Applicant has previously pointed out that the example oils disclosed in Cohen have a sulfur content of 200 ppm or 300 ppm and %C_A of 14 or 12 (Cohen, col. 3, Table 1); and if these oils are filtered to reduce sulfur and nitrogen contents and the respective concentrations of both sulfur and nitrogen have been reduced to level of 50 ppm or lower, %C_A must also be reduced to be out of the claimed range of 8-15 (perhaps down to 0). *See* October 26, 2010 Reply to Office Action, page 8; May 13, 2010 Reply to Office Action, page 9.

This Applicant's position is corroborated by the attached learned Treatise, "LUBRICANT AND SPECIAL FLUIDS," Vaclav Stepina et al., Tribology series 23, pages 134-147 (1992). The document describes that hydrogenation is one of the known procedures for refining mineral oils (page 139), and changes the compositions of

the mineral oils, e.g., sulfur content (%S) and aromatic content (%C_A, RA) are reduced by hydrogenation (page 141). As an example, Table 3.4 at page 142 of the document shows that the value of %S of original oil is reduced from 1.18(before) to 0.063 (after), and that the value of %CA of original oil is reduced from 20.3 (before) to 5.1 (after). The document therefore supports that the concentrations of sulfur and %CA could not be adjusted independently; a decrease in sulfur content would affect %C_A.

For these reasons, if the example oils disclosed in Cohen having a sulfur content of 200 ppm or 300 ppm and %C_A of 14 or 12 (Cohen, col. 3, Table 1) are filtered such that the sulfur contents are reduced to "no more than 48 ppm," as recited in claim 13, then %C_A must be reduced to be out of the claimed range of 10-15 (perhaps down to 0). Accordingly, Cohen neither discloses nor suggests a mineral oil as recited in claim 13.

For at least the above reasons, claim 14 is allowable over Cohen in view of Shimomura.

IV. CONCLUSION

In view of the foregoing remarks, Applicant respectfully requests reconsideration of this application, withdrawal of the rejections, and timely allowance of the pending claims.

Should the Examiner have any comments or questions, please contact the Applicant's representative at (202)408-4457.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account 06-0916.

Respectfully submitted,

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Dated: April 7, 2011

By: _Hojung Cho_

Hojung Cho
Ltd. Rec. No. L0596

Attachment: "LUBRICANT AND SPECIAL FLUIDS," Vaclav Stepina et al., Tribology series 23, pages 134-147 (1992).

Tribology series, 23

UDC 621.89
621.892.554 ©

LUBRICANTS
AND
SPECIAL FLUIDS

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and higher polarity resins remain undissolved as a heavy phase. Selectivity can be controlled by adjusting the propane: asphalt ratio (as high as 10:1) and the temperature (up to 80 °C). n-Butane, which is less selective, can also be used. After the propane had evaporated from each of the two phases, the heavier oil (propane-deasphaltenes or brightstock) and propane asphalt are isolated. The process amounts to a selective extraction by a non-polar solvent.

Industrial exploitation has started off extractive distillation of oil residues by gases in a critical state. It makes use of the earlier described principles of fluids process. In this case, supercritical gases the transport and diffusing properties of gases together with the solvent properties of liquids. This is true of non-polar fluids, e.g. methane to butane, as well as polar ones, such as toluene, carbon dioxide and ammonia [257, 258, 259].

Carbon dioxide dissolves, at 7.3 MPa and 31 °C the non-asphaltic parts of distillation residues and liberates them again when the pressure is lowered and the temperature is raised. This procedure (sometimes termed detraction) is also suitable for extracting the non-asphaltic components from tars and from coal hydrogenation residues, for separating oil from used oils or from heavy crude oil deposits or asphalt sands [259].

3.2.1.2.3 Refining Processes

Refining substantially changes the chemical composition of lubricating oil distillates and can thus control the properties of softness [10, 259]. Its primary effect is to reduce the concentration of the most polar constituents -oxygen, nitrogen and sulphur compounds, poly-nuclear aromatics and - to the extent that they are present - olefinic hydrocarbons, the products of fond over-heating. The object of refining processes is to improve colour, VI, long-term stability against ageing in storage and at operating temperature, the reduction of coking, etc. Unless refining is accompanied by profound chemical transformations (e.g., as in hydrogenation), distillation ranges and flash-point do not change significantly. Pour-point may rise somewhat if the paraffin wax crystallisation inhibitors (some resins) are removed, or if transformation into n-alkanes or long-chain alkyl substituents occurs. However, it may decrease in the event of isomerisation or cleavage of n-alkanes or n-alkyls takes place. In contrast to distillation, both density and viscosity decrease. Alterability to treatment with additives improves.

etc. The ASTM D-156 method is also suitable for determining the colour of "white" oils.

Another criterion is the amount of residue produced on "carbonisation". This type of test consists in determining the percentage of solid formed by thermal decomposition of the oil in the absence of air. The carbonisation residue is determined by the formal decomposition of a 10 g oil sample in a porcelain crucible under prescribed heating conditions. The CCR carbonisation test is identical to the CCT, except that a 2 g sample is used in a similar porcelain crucible.

The main types of refining processes now employed are refining with chemical agents, selective solvents, adsorbents and hydrogen (hydrogenation), which refining is described elsewhere in this book.

Refining with Chemical Agents [10c]

This is the earliest refining process. The main agents used are sulphuric acid and sometimes oleum or sulphur trioxide, or, more rarely, other agents such as anhydrous aluminium trichloride [10d]. Refining with acid agents is followed by neutralisation, usually with calcium hydroxide or caustic alkali.

Sulphuric acid causes polymerisation, condensation and, at elevated temperature and concentration, sulphonation and oxidation. It also partly acts as a selective solvent. Saturated and mono-nuclear aromatic hydrocarbons are comparatively unattacked. The unsaturated components, e.g. thermally-damaged lubricating oils, produce acidic esters and polymers, which pass into the acid layer. Poly-nuclear aromatics tend to undergo condensation and sulphonation; the products of these transformations also pass into the acid layer. The same applies to all resins and nitrogenous compounds, oxygen and sulphur compounds. They partly dissolve in the acid, are partially converted into bank species, condense or are sulphonated. The non-aromatic naphthenic acids dissolve in the acid, whilst the aromatic ones can, additionally, be sulphonated. Nitrogenous bases are neutralised and pass into the acid. However, the selectivity of these processes is rather poor.

The process produces two layers: a less polar raffinate and a layer of acid sludge (acid resins). The layers are separated by settling, centrifugation or electrostatic processes. The raffinate is extracted with caustic alkali and washed with water. After drying, it may be further show good quality parameters, although the VI is not raffinate. This is a product showing good quality parameters, although the VI is not much higher than that of the distillate. The acid sludge is a troublesome waste. It is hard to handle, corrosive and undergoes further condensation and oxidation reactions connected with the liberation of sulphurous. Disposal procedures are still not satisfactory, which is one inhaling sulphur dioxide. Disposal

of the reasons why no new plants are being erected. Existing plants, as long as they continue in operation, are used for the production of light bearing, turbine, transformer and similar lubricants from wax-free or de-waxed distillates.

Refining Used Oils

Refining with sulphuric acid until is also used for reclaiming used engine and some lubricating oils [2]. Reclaimed oils may achieve composition and attributes similar to the original oils, however, their refining is somewhat troublesome. Most of the problems stem from the presence of physical and chemical ageing and by contaminants and additives present. One of the procedures worth mentioning is the Czechoslovak process which involves the transport of these contaminants into a water-glass solution, whereby the contaminants are adsorbed on the colloidal silicic acid produced by hydrolysis in the water layer [27]. Waste oils may also be decolourised and deodorised with adsorbents, e.g., oxyethane phenol, and after sedimentation or conventional acid treatment [28]. However, even for the treatment of waste oils, sulphuric acid processing is being replaced by other processes, such as solvent treatment, hydrogenation or combinations of these [29].

Modern reclaiming technique based on combined distillation, desphalting, solvent refining and, chiefly, hydro-refining processes are capable of producing reclaimed oils which match the quality of virgin refinates. The quality of a reclaimed oil used in engine lubricants is shown in Table 3.2.

Table 3.2. Quality Specification for a Re-refined Used Engine Oil

Parameter	ASTM Method	Limits
Flashpoint	D92	as in virgin sulfuate
Insoluble Substances	D893	0.01% by weight max.
Sulphated Ash	D874	0.01% by weight max.
Glycols	D2982	negative, except for the blank test
Sulphur	D129	0.25% by weight max.
Pourphous		50 p.p.m. max.
Chlorine		100 p.p.m. max.
Water	D95	0.05% max.
Neutralisation No.	D664	0.1N TAN num., strong base,0, strong acids, 0.
Alkaline Point	D-611	93 °C min.
Viscosity Index	D-2270	95 min.
Trace Metals	X-ray fluorescence, atomic absorption, or emissive spectroscopy	90 min.

The Manufacture of White Oils

Medicinal oils must not contain aromatics. Fuming sulphuric acid and, more recently, sulphur trioxide are used for their manufacture, as well as for the manufacture of technical white oils. After pre-treatment with acid and removal of the acid sludge, or after a pre-treatment with hydrogen, the aromatics and resins are suppressed by repeated dosages of oleum or SO_3. The sulphonic acids formed pass partly to the oil and partly to the acid layer. The oil layer is extracted with an alcoholic solution of caustic alkali. The "technical" or "heavy" sulphonates are salt-like substances soluble in water and form the basis for the manufacture of detergent additives for oils and emulsifiers. The "green" sulphonates extractable from the water layer are inferior but cheap wetting agents. Again, in the manufacture of white oils, hydrogenation is displacing acid-refining if sulphonates are not required [22].

Solvent Refining

The main criterion of solvent power is similarity of chemical composition or of molecular mass.

Solvent refining consists in the separation of wax-free oil cuts into two layers: one rich in less-polar components, poor in solvent, the raffinate layer, the other rich in polar components and solvent, the extract layer. After flashing off the solvent, the raffinate comprises the high-grade part of the original oil, characterised by high VI (up to 100, but rarely more), light colour and high stability against ageing whilst the extract is that part with undesirable attributes (with low compound), dark colour, even negative VI, low resistance to ageing and a tendency to form carbonisation residues.

Solvents are selected according to their selectivity and solvent power. Selectivity is that property which distinguishes between wanted and unwanted components and provides the means to separate them; solvent power defines the quantity of solvent necessary to transfer the more soluble components into the extract. Both properties change with increasing temperature: selectivity decreases, solvent power increases (with a few exceptions, e.g., propane in the deasphalting process). At the critical temperature, one phase is formed and no separation occurs. Thus, by changing the temperature and the solvent to oil ratio, the desired depth of refining can be achieved.

The most common solvents are furfural (FF), suitable for all oil stocks (even gas oil and bright stocks), and phenol (Ph), more used for waxy oils that wax-free, and for more heavy than light cuts. More recently, N-methylpyrrolidone (NMP) has also been used. It has good selectivity (FF > NMP > Ph), biodegradability (NMP > Ph > FF) and lower toxicity. This all leads to lower investment and operating costs, so that many furfural and phenol refining plants are being converted to NMP (QM). Other solvents are known (e.g. wet bitercril, SO_2, benzene), but they have only found limited application or are now regarded as out-dated.

Solvent Precipitation

In selective precipitation processes, non-polar solvents precipitate the most polar asphaltenes and oil resins in oil distillates and distillation residues, in oils to deasphaltened wax components (as in semi de-waxing processes), and finally to remove products and additives from used oils. The less polar or light constituents are transported into the solvent. Conventional precipitants are alkanes, chiefly liquid propane. The lighter alkane precipitates too much of the oil with the asphalt, re-... and the most condensed resins of highest softening point. The effects of both polar and non-polar solvents may be combined in one unit operation. Thus, in the Duosol process for distillation residues, asphaltenes and resins are precipitated by propane and the propane simultaneously extracted with a phenol-cresol mixture.

Adsorption Refining Processes

Adsorption refining is based on the adsorption of polar substances on the surface of a polar adsorbent, for example, natural or synthetic aluminosilicates, silica gel, alumina or bauxite. These processes nowadays are mainly used for reclaiming used oils after acid or solvent refining to remove refining spent and other impurities and colour. Although it is possible, in adsorptive refining, to separate the desirable from the undesirable oil components better than with solvent refining, and to obtain higher yields of raffinate, it is rarely employed as the main refining process (J5).

Adsorptive refining with high surface area graphite may become the exception. Here the softeners (oil waxes) and polyaromatic aromatics are primarily adsorbed. Oils of substantially higher VI and, particularly, low viscosity at low temperatures are recovered (J10).

Adsorptive refining is classified into contact and percolative processes. In contact processes, the oil is mixed with a minor proportion of the finely divided adsorbent (1–3%) at below 100 °C in the cold-contacting process, before separation of the spent adsorbent. This variant is used for cleaning light industrial oils (toeline oils, electrotransmitting oils, etc.) as well as reclaiming these oils. The hot contacting process proceeds at temperatures up to 340 °C to the flash-point of the oil but never above its decomposition temperature, with the object of achieving more thorough reclaiming of engine oils, compressor oils and, generally, heavy oils and brightstocks.

Percolation processes consist in filtering the oil at lower temperatures through a stationary bed of relatively coarse-grained adsorbent and recovering the first clusters, which becomes gradually darker as the production proceeds. The later clusters are returned to the old-stock feed-tank.

Adsorptive refining improves oil colour, brightness and oxidation stability, and removes water and contaminants which might be corrosive.

Adsorption processes used to be common in the final treatment before oil-blending to required quality. Problems of disposal of spent adsorbent have contributed to their replacement by hydrogenation processes.

Hydrogenation (J6s)

Unlike acid refining and solvent refining, hydrogenation produces various depths of conversion of undesirable components into lighter, low-viscosity and heavier, high viscosity hydrocarbons. No troublesome wastes are produced.

Three types of hydrogenation process may be distinguished: hydrofinishing, hydrofining and high-pressure hydrogenation or mild hydro-cracking. All three types proceed at higher temperatures, from 250 to 420 °C and at pressures from 2 to 20 MPa, both parameters higher and lower in exceptional cases due to the use of catalysts, which are usually transition metals and their compounds (oxides, sulphides) on a more or less acid substrate. In a hydrogen environment and with the consumption of hydrogen. In the hydrofinishing processes, the best traces of impurities remain in the oil after acid or solvent refining are removed in hydrofining, some deeper transformation occur, including partial saturation of aromatic and partial hydrogenation of O, S and N-containing components. In high-pressure hydrogenation, at the upper temperature and pressure limits – virtually a mild hydrocracking process – deep transformation occur, almost complete hydrogenation and hydrogenolytic reactions, isomerisations and cracking reactions.

Hydrofinishing and Hydrofining

Typical operating conditions for these processes are temperatures of 250 to 370 °C, pressures from 2 to 7 MPa, liquid-hourly space velocities (LHSV) 0.5 to 3 h^{-1}, hydrogen-to-feed ratios 300 to 800 vol./vol. for hydrofinishing. Typical catalysts are cobalt molybdate or more active nickel and nickel-cobalt molybdates on a slightly acidic alumina (e.g., 10 to 15% MoO_3, 1 to 5% CoO, 4 to 5% NiO) for hydrofinishing and less in hydrofining. The light by-products are flashed off within the unit.

In hydrofinishing, no substantial chemical transformation take place. In hydrorefining substantial reduction of oxygen compounds and of 20 to 70% of sulphur compounds (in terms of sulphur content) occurs - hence the synonymous designation hydrotreating/hydrosulation. Nitrogen compounds are troublesome, heavy compounds being more difficult to transform than light compounds. Saturation and destruction of oil content in the catalyst. Resin concentration is reduced, as is carbonisation residue (up to 50%), colour is improved, viscosity slightly reduced and VI slightly increased. Stability to ageing and additive response are increased, in this respect, medium pressure hydrogenation is a mild refining process which normally follows, but may precede, solvent refining of oil distillates.

High-Pressure Hydrogenation - Hydrocracking of Oils

The importance of HP-hydrogenation as the main treatment of lube oil distillates or deasphalted distillation residues is increasing. It enables oils to be obtained with a high VI or even extremely high VI (XHVI - e.g. up to 150 from hydro-cracked slack waxes). This process was probably first introduced under field conditions in Czechoslovakia in 1961: about 40% of lube oils are now products of HP-hydrogenation. Typical operating conditions are temperatures 370 - 420 °C, pressure 10 - 30 MPa, LHSV 0.5 - 1.5 h⁻¹, hydrogen-to-feed ratio 900 - 2,000 vol./vol. and consumption of hydrogen 80 - 250 vol./vol. Even at the same VI, the composition of hydrocracked oil differs significantly from that of solvent refined oil, as shown by Table 3.3 (21, 209). Catalysts used are more active than those in hydrofining, being mostly sulphides of transition metals, like MoS_2, WS_2, or natural or synthetic stocks like Ni, Pd, Pt, all on γ- or η-alumina molecular sieves [H-AlSiO₄/H] (21, 22). Two directions and the acidity of the catalysts are carefully balanced so as to impede rapid deactivation and to guide the transformation in the desired direction. The metallic component enhances hydrogenation, leading to cyclohexanes and alkylated and cycloalkylated benzenes from O, S and N constituents, resin, polynuclear aromatics to a certain extent polycycloalkanes [24]. The noble metals enhance the hydrogenolytic opening of cycloalkane rings to branched-chain alkyls. The acidic component facilitates cleavage, producing hydrocarbons with lower viscosities and the isomerisation of cycloalkanes to cycloparaffins and to branched, saturated hydrocarbons with lower pour-points. It also enhances the hydrocracking of substances with electron-donor properties. In the acid regions the hydrocracking of heavy sulphur adsorption on to electron-acceptor centres. However, this increases the risk of catalyst deactivation by carbonaceous products (so that pore dimensions must be optimised (22)).

Hydrogenation is thermodynamically a low temperature process, but its kinetics require higher temperatures. This contradiction must be compensated by higher pressures. Active catalysts permit temperatures and pressures to be decreased. Under

otherwise identical conditions, an increase in temperature increases hydrogen consumption and affects the composition of the hydrogenate (22). Reducing the pressure, under otherwise identical conditions, cause hydrogen consumption to decrease, prolongs the operating cycle, but adversely affects the hydrogenation of aromatic hydrocarbons and heteroatomic components, so that the residual concentration of heavy aromatics and resins in the product is higher. So to achieve products of the same VI with less active catalyst, the temperature must be raised. Hydrogenation changes the composition of all hydrogenate oil groups (20) - see Table 3.4 and 3.5. The viscosities, densities, sulphur content (%S) and aromatic content (% C_A, R_A) are all reduced, whilst VI, hydrogen content, paraffinic-cycloalkane compounds and rings (% C_P, R_P) are increased. The raw (paraffinic) pour-point of oils are increased, whilst the false (viscosity) pour-point are decreased. This suggests that it may be advantageous to subject to HP-hydrogenation those stocks which are roughly unified as a group in terms of their constituents, and use processes which simplify the composition of the feed, e.g. hydrofining, or to proceed on more than one page.

Table 3.3. Comparison of Duo-Sol Solvent Extraction and Hydrocracking of Romashkino-Mukhanovo Crude [?]

	Duo-Sol Solvent Extraction	Hydrocracking
Viscosity (mm²/s) at 50°C	31.31	35.13
VI	90	91
Pourpoint (°C)	-12	-10
Chemical Composition by Mass Spectrometry, % w/w		
Monoparaffins	20.2	21.1
Monocycloalkanes	5.6	12.7
Dicycloalkanes	11.3	16.4
Higher Alkanes	28.5	31.6
Total Cycloalkanes	45.4	60.7
Alkylbenzenes	5.5	4.9
Indanes + Tetralins	2.6	3.2
Diphenylmethanes	3.6	2.2
Naphthalenes + Triphenylmethanes	2.2	0.8
Anthracenes + Acenaphthenes	4.2	1.5
Fluorene + Acenaphthenes *		
Decylbenzothiophenes	2.9	2.0
Total Aromatics	26.7	17.8
Benzothiophenes	3.8	0.0
Dibenzothiophenes	6.5	0.0
Resins	1.2	0.4

* Relative data.

Table 3.4. Changes in the Composition and Properties of an Oil and Its Chromatographic Constituents - before and after Hydrocracking (24)

Oil	original		alkanocyclane		monoaromatics		diaromatics*		polyaromatics*	
	before	after	before	after	before	after	before	after	before	after
Yield (% vol.)	100	100	38.8	71.9	26.8	16.2	17.7	6.45	9.7	0
Density at 20 °C (kg.m⁻³)	949	879	856	856	899	898	995	987	1049	—
Viscosity at 50 °C (mm².s⁻¹)	53.4	24.3	22.8	20.0	31.7	22.4	157.5	71.0	736	—
VI	58	91	107	121	68	68	-122.	50	-415	—
%H	12.4	13.0	14.1	14.0	12.03	12.93	10.8	11.2	9.81	—
%S	1.18	0.063	0.033	0.0015	0.67	0.063	2.89	0.472	3.13	—
Pour-point (°C)	-18	4.5	-9	6.2	+17	17.5	8	-13.5	12	—
Composition by Type (ndM)*										
%C_A	20.3	5.1	0	0	15.0	155.1	40.9	33.3	44.8	—
%C_N	20.7	36.4	29.4	20.7	22.6	25.2	18.1	29.4	34.5	—
%C_P	59.0	58.5	70.6	69.3	62.4	59.7	41.0	37.3	30.7	—
R_C	2.18	2.37	1.86	1.82	2.39	2.52	4.04	3.53	5.20	—
R_A	1.08	0.21	0	0	0.80	0.77	2.68	1.68	2.58	—
R_N	1.58	2.16	1.80	1.82	1.59	1.75	1.36	1.85	2.62	—

* Diaromatics and Polyaromatics according to Hazelwood.

Table 3.5. Changes in Viscosity, Viscosity Index and Chemical Composition at Increased Hydrogenation Severity (21)

	Hydrocracked Oils from Vacuum Distillate				Hydrocracked Oils from Propane Deasphaltate		
Viscosity Index	91.2	98	115	123.5	83.5	121	127
Viscosity (mm².s⁻¹) at 50 °C	35.13	28.15	22.94	19.9	88.27	35.92	29.63
Chemical Composition by Mass-Spectrometry (% weight)*							
Alkanes	21.1	22.4	28.7	43.1	15.1	37.5	32.8
Monocycloalkanes	12.7	21.6	26.7	19.5	17.4	21.7	29.0
Dicycloalkanes	16.4	19.1	19.6	10.2	9.5	18.0	18.4
Higher cyclanes	31.6	16.0	12.3	6.0	23.1	7.6	8.3
Cyclanes	60.7	56.7	58.6	35.8	50.0	47.3	55.7
Alkylbenzenes	5.5	9.0	6.4	7.0	17.2	9.3	4.9
Indanes + tetralins	4.1	4.7	2.5	5.4	7.5	2.5	3.8
Dicyclanobenzenes	3.2	3.3	1.4	2.3	5.1	1.2	0.9
Naphthalenes + tricyclanobenzenes	0.8	1.0	0.4	0.8	1.7	0.4	0.4
Acenaphthenes + diphenyls	2.3	0.8	0.7	1.5	1.2	0.6	0.6
Fluorenes + acenaphthalenes + dicyclanonaphthalenes	2.0	1.8	0.8	1.5	1.8	0.7	0.1
Aromatics	17.9	20.6	12.2	18.5	34.5	14.7	10.7
Resins	0.4	0.3	0.5	0.6	0.4	0.5	0.8

* Relative data.

HP-hydrogenation (i.e. mild hydrocracking) enables high-grade and high-VI oils to be produced economically. Oils of this quality cannot be obtained by solvent refining, and even if they could, yields would be very low. The superiority of HP-hydrogenation consists in the possibility of obtaining oils with VI's up to 130 (exceptionally even higher) from almost any type of oil in high yields, in better response to additives, lower volatility and better biological properties. Undesirable constituents are removed or converted to substances that improve the oil's characteristics, e.g. by aromatics saturation. The oxidation and thermal stability are above average; yet the oils react well to oxidation produces and additives.

The overall concentration of aromatic compounds, together with the concentration of sulphur and nitrogen compounds, are decisive factors in the properties in service of HP-hydrogenates, particularly in respect of thermooxidative stability. This stability grows up to a certain critical concentration of aromatics, when this it becomes much worse [166, 260]. The relative molecular mass of the aromatics, the number of fused aromatics and the greater the concentration of sulphur compounds, the lower is the critical concentration [176, 177]. Hydrogenates containing less than 5% of aromatics have a rather poor oxidation stability. In comparison with selective refinates, hydrogenates are especially sensitive above 210–220 °C. This manifests itself by a tendency towards more serious carbon deposition in the first piston grooves with engine oils formulated from hydrogenates. This inconvenience may be overcome by optimising the structure and content of additives (anti-oxidants, detergents and dispersants) or using doped blends of selected refinates and HP-hydrogenates.

Oils made from HP-hydrogenates is low solvent power for additives, particularly for some polymers, and for the polar products of ageing. This is due to the low concentration of aromatic compounds, which is also responsible for a high aniline point of HP-hydrogenates and for shrinkage of rubber seals and packings (aromatic content which is too high causes swelling).

A further drawback associated with HP-hydrogenates is low solvent power for additives, particularly the less readily soluble ones. This is disadvantage to be overcome [172].

Pale-coloured sludges are formed in hydrogenated oils by the action of light. The constituents which are responsible for this effect have not yet been identified, but compounds with a reactive tertiary carbon, traces of olefins originating from dehydrogenation, or some hydroaromatic of polynuclear compound are suspected. Light stability can be improved by removing or converting these components, e.g. by low-temperature hydrogenation after-treating in a fine-finishing converter; by catalytic conversion on molecular sieves in the absence or presence of added diluents [226] (which also improves resistance to ageing); by further reducing the concentration of heavy aromatics by clay treatment; and by using suitable anti-oxidant, because the natural anti-oxidants (some resins, some poly-nuclear aromatics) have to a large extent been removed.

The preferred feedstocks for HP-hydrogenation include heavy oil distillates, desphalted vacuum distillation residues and, more recently, distillation residues from high-severity cracking to make motor fuels. Slack waxes may even be hydrocracked to XHVI oils. Specific processes have been developed [262]. Some have been commissioned or are being promoted in the USA (Chevron - 261), France and Germany (the IFP process - 262), the Soviet Union (260), East Germany (264) and in Czechoslovakia (the NIVOL process - 265). Yields up to 30% of viscous hydrogenating brightstocks. So a wide variety covering almost 98% of the lube oil range can be produced, with the exception of heavy compressor and cylinder oils - medium distillates or hydrogenates for bearing, turbine, hydraulic, transformer, white and similar oils and heavier hydrogenates emanating from hydrogenated brightstocks of improved with suitable additives as with predominantly distillates of engine oils recovered with similar refining efficiency. As by-products, saturated and virtually aromatic-free minor fuels and refined waxes with improved filmability are obtained. HP-hydrogenates are serious competitors of synthetic polyalphaolefin (PAO) oils, with the advantage of lower price.

De-Waxing Processes

Solvent dewaxing is the dominant process in the recovery of oils of low pour-point and good rheological properties at low temperatures from waxy distillates and raffinates. The oil is diluted with the solvent, chilled to low temperature and the separated wax crystals filtered off [107].

Suitable solvents include propane, particularly for producing oils of very low pour-point, or so-called solvent/antisolvent mixtures. The anti-solvent precipitates the wax and the solvent dissolves the oil which is excluded in the filter cake. Examples of anti-solvent/solvent pairs are: methylethyl ketone (2-butanone)-toluene and 1,2-dichlorethane-dichloromethane. Precipitating and dissolving effects are combined in methylisobutyl ketone (4-methylpentan-2-one).

Light oils may also be de-waxed by molecular sieves, formation of urea adducts with dilutes adsorption of n-alkanes by molecular sieves, formation of urea adducts with dilutes adsorption of paraffins by fermentation. These processes are of limited importance.

Oils are extremely low pour-points and low viscosities at low temperatures (for bearing, hydraulic, transformer and other oils) are still mostly manufactured from refining wax-free cycloalkanic oil oils. Oils with similar properties may also be

obtained by de-waxing waxy cuts at very low temperature. Since the latter method is expensive, the base oils are processed based on combinations of conventional de-waxing and the further decrease of oil pour-points and viscosities at low temperatures by adding pour-point depressants have been developed. The advantage of such a procedure is that the oil produced in this way have lower viscosities at low temperatures than oils made from cycloalkane crudes and that they retain relatively high VI's and the required pour-points.

These base pour-point oils, however, have limited applications. They cannot be used in service where there is the presence of refrigerants at a minimum, e.g., for the lubrication of refrigerating compressors, particularly those of the Freon type.

Catalytic de-waxing processes have been developed recently (264, 265). Low pour-points are achieved by isomerisation and hydrocracking of constituents with long alkyl-chains at about 360 °C and pressures up to 10 MPa, in the presence of hydrogen and hydrogenation catalysts (Pt, Pd, Ni, etc.) on acidic molecular sieves with pores which allow the adsorption of straight-chain hydrocarbons, e.g. mordenites is the H-form. Light oil-cuts, e.g., from HP-hydrogenation, are similar feed-stocks, and the product - obtained in 70-80% yields - has pour-points down to -40 °C and lower. The by-products are gases and light liquid hydrocarbons.

Lubricant Base Stocks

The processes described earlier are used for the production of base oils for several different types of lubricating oils. These oils are nowadays regarded as being sorted into conventional types, and essentially classified into three group headings, each group being capable of further improvement with additives.

A. High viscosity index raffinates, designed mainly for high quality engine oils and some special types of industrial oils (Table 3.6).

B. Medium viscosity index raffinates, used either alone or in blends with the above oils for light quality industrial oils and greases (Table 3.7).

C. Low viscosity index raffinates, suitable for some types of industrial oils, where the viscosity-temperature characteristics need not be considered and where thermooxidative stability is not decisive (Table 3.8).

3.2.2 Synthetic Oils

Although modern types of mineral oils reinforced by additives are capable of meeting a broad range of lubricating and other requirements, their properties are in some cases significantly surpassed by those of synthetic oils, for example, where very low or very high temperatures prevail, or under conditions where a wide operating temperature range or an unconventional environment, e.g., ignition hazard or exposure to ionising radiation, impose unusual requirements (30, 31, 32). Notwithstanding their limited availability and high price, these base fluids, synthetic oils find application and are occasionally viable. Various types of synthetic oils are suitable for use in admixture with mineral oils - the so-called "semi-

Table 3.6. High Viscosity Index Raffinates

Parameter	Solvent Neutrals*							Brightstocks‡	
	100	150	200	350	400	500	600	100BS	150BS
Viscosity at 100 °C (mm².s⁻¹)	4.1–4.6	5.2–5.6	6.3–6.7	9.2–9.6	10.0–10.5	12.3–13.5	14.2–15.0	20.0–21.2	31.5–32.5
Viscosity Index (min.)	100	97	97	95	95	95	95	95	93
Flash-point									
(P.M., °C min.)	190	200	215	220	230	230	240	255	265
(O.C., °C min.)	230	230	240	245	250	250	260	280	295
Fire-point (°C, min.)	245	245	265	270	275	275	300	320	320
Pour-point (°C, max.)	-17	-15	-12	-9	-9	-9	-9	-9	-9
CCT (% wt, max.)	0.02	0.03	0.05	0.1	0.1	0.1	0.15	0.6	0.8
Colour (ASTM, max.)	1.5	1.5	2.0	2.5	3.0	3.0	3.5	6	6
Colour stability††									
(48 h, 100 °C, max.)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Acidity (mg KOH/g, max.)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Ash (%wt, max.)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Clouding by separated paraffins after 3 months at 20-25 °C								no haze produced	

* Conventional term for fully-refined oils of low acidity; the numbers represent average values of viscosity in SSU at 37.8 °C.
‡ Conventional term for raffinates from deasphalted petroleum distillate residuum.
†† Deterioration of oil colour at 100 °C after 48 hours exposure to light.